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(54) **Spray urethane elastomer.**

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## Description

The present invention relates to a process for manufacturing a spray urethane elastomer, and more particularly to a process for manufacturing a solventless spray urethane elastomer prepared from a prepolymer component obtained by a specific formulation and a resin component by use of a two component, high pressure, spray machine.

Conventional manufacturing processes for spray urethane elastomer include, for example, a solvent dilution process (in Adiprene Bulletin by Du Pont de Nemours) which process comprises dissolving a prepolymer having a terminal isocyanato group and a highly active aromatic amine curing agent such as diphenylmethanediamine and the like separately in a solvent and coating by use of a conventional two components spray machine at a pressure of about 70 Kg/cm<sup>2</sup>. Another process comprises diluting in a solvent and mixing the above prepolymer and a low active aromatic amine curing agent such as 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) and the like, followed by spraying within a pot life by use of a high pressure one component spray machine (see Japanese Patent Application Laid-Open No. 17430/74 by MITSUI TOATSU CHEMICALS, INC.). Yet another process uses a high boiling solvent which remains in the coated product. A further process comprises reacting a partial prepolymer with a mixture of a high molecular weight polyol and a low molecular weight polyol (see Japanese Patent Application Laid-Open Nos. 134077/75 and 147329/75 by MITSUI TOATSU CHEMICALS, INC.).

The above processes raise environmental pollution problems due to the use of the solvent, thermal energy losses due to forced heat curing in the case of a thick-coating, and problems of developing a large amount of foam from the coated product in the case of one-time thick-spraying because of the need to evaporate the solvent from the coated product. The process which uses the high boiling solvent to prevent foams from developing and allows the solvent to remain in the coated product, raises that the solvent is lost when the coated product is used over a long period of time due to migration, evaporation, or elution into rainwater and the like, resulting in deterioration of the coating taking place along with cracking, shrinkage, etc.

A process, in which coating is carried out thinly and repeatedly, takes a long period of time to accomplish.

A process in which, for example, a carbodiimide modified liquid diphenylmethane diisocyanate (hereinafter diphenylmethane diisocyanate is referred to as MDI) or a partial prepolymer of MDI is reacted with a mixture of a high molecular weight polyol or a low molecular weight polyol to prepare a coated product, has drawbacks that the low molecular weight polyol is so highly hygroscopic as to result in a competitive reaction between the hydroxyl group and moisture, is easily foamed, develops pinholes, craters and the like on the coated product, and reduces the specific gravity and strength of the coated product.

The above processes all have such drawbacks such as reduction in density of the coated product, and consequently deterioration in physical properties, deterioration in surface properties, etc., because of foaming due to moisture in the air and foaming due to moisture caused by hygroscopicity of the polyol component.

Conventional processes for manufacturing urethane elastomer include such ones as cast moulding, millable polyurethane process, thermoplastic moulding, etc. It is very difficult for the above processes to be applied to a lining in order to impart abrasion resistance, etc. to a surface having a complicated configuration.

Publication WO87/07287 describes a process for making a solventless urethane elastomer by using a high pressure spray machine. This spray machine is fed with a mixture of a first component which may be an isocyanate terminated prepolymer and a second component which may be a mixture of a polyamine, a blend of a high molecular weight polyol and a low molecular weight glycol, and a catalyst. We have found, however, that the presence of the low molecular weight glycol, reduces the reaction rate to unacceptably low levels for spray moulding and gives a cheese-like appearance on curing which can cause cracks and the like in the finished coating.

According to the invention there is provided a process for manufacturing a solventless spray urethane elastomer which comprises spraying directly onto a substrate, by use of a two components high pressure spray machine with a colliding and mixing type spray gun under a pressure of 60 to 150 kg/cm<sup>2</sup>, in a NCO/OH molar ratio of 0.9 to 1.3 of the undermentioned components A and B:

Component A - a partial prepolymer component prepared by reacting an organic polyisocyanate and a polytetramethylene ether glycol having a molecular weight of 400 to 2000 or a mixture of polyols which consists of the polytetramethylene ether glycol and from 1 to 20% by weight of the polytetramethylene ether glycol of a low molecular weight glycol selected from dipropylene glycol, tri propylene glycol, tetrapropylene glycol,

diethylene glycol, 1,3-butanediol, 1,4-butanediol and neopentylglycol, at a NCO/OH molar ratio of 5 to 40.

Component B - a resin component prepared by mixing a polytetramethylene ether glycol having a molecular weight of 400 to 2000, a chain extender which consists of an active aromatic polyamine which is free of an electron attractive group on the aromatic nucleus, an organobismuth compound as a catalyst,

and optionally, one or more of :

(i) one or more plasticizers selected from dioctyl phthalate, dibutyl phthalate, dioctyl adipate and chlorinated paraffin,

(ii) one or more flame-retardants selected from phosphoric acid esters and bromine compounds,

(iii) a stabiliser in an amount of from 0.3 to 2% by weight of the resin component, and/or

(iv) a filler,

the proportion of glycol being at least 70% by weight, of polyamine being at least 10% by weight, and of catalyst being from 0.2 to 2% by weight.

By following the present invention, and spraying only the stock solutions by use of the two components high pressure spray machine one can achieve coatings and the stock solutions are cured in one second to ten and several seconds after being sprayed without producing cells even when thick-coated. Therefore, the present invention makes it possible to effect wet-on-wet coating within a short period of time, resulting in making it possible to accomplish a final coating having a predetermined thickness in a short period of time.

The elastomer, which has been coated, has excellent modulus, tensile strength, elongation, tear strength, heat resistance, and the like. It can be used to coat pipes, tanks and the like, provide waterproof coatings such as on concrete for a roof or outside wall which needs waterproofing, can provide thick-coated protective coatings for thermal insulating purposes on rigid polyurethane foam, polystyrene foam, board or the like, can provide a seamless floor covering material, and can be open mould moulded by use of a mould made of for example metal or resin.

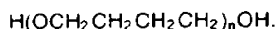
The process according to the invention provides a spray urethane elastomer which is capable of being thick-coated and is free of the influence of moisture. Also the resulting elastomer has the excellent physical properties, particularly high abrasion resistance.

The moulding process by spraying according to the present invention makes possible mouldings and applications which have previously been considered impossible. Thus, the process of the present invention is capable of being applicable to a vertical surface because of a high initial curing speed, completely preventing cracks from developing by preventing cheese-like jellification which initially takes place, and obtaining a moulded product having satisfactory physical properties.

The reaction rate of the starting material system in the present invention is so high that the conventional stirring machine is unusable and a special spray machine is needed. It is an essential requirement that a two components high pressure spray machine is used, that respective hydraulic pressures are raised up to at least 60, and preferably about 100, kg/cm<sup>2</sup>, followed by mixing with a colliding and mixing gun, and immediately followed by spraying.

Examples of the organic polyisocyanate which can be used in the present invention include 2,4-tolylene diisocyanate (hereinafter referred to as d,4-TDI), 2,6-TDI and a mixture of 2,4-TDI and 2,6-TDI, 2,4'-MDI, 4,4'-MDI and a mixture of 2,4'-MDI and 4,4'-MDI, xylene diisocyanate (XDI), 2,4-and/ or 4,4'-dicyclohexylmethane diisocyanate (hydrogenated MDI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), hydrogenated xylene diisocyanate (HXDI), crude TDI, polymethylene polyphenyl polyisocyanate (crude MDI, polymeric MDI), isocyanurate-modified ones, carbodiimide modified ones, biuret modified ones and urethaneimine modified ones of the above isocyanates respectively. Of the above organic polyisocyanates, MDI, crude MDI and their modified ones are particularly preferred.

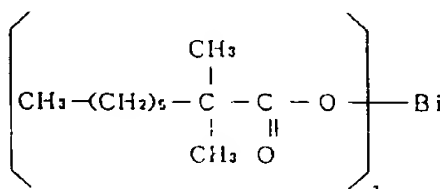
The polytetramethylene ether glycol (hereinafter referred to as simply PTMEG) having a molecular weight of 400 to 2,000 used in the present invention is a diol obtained by the ring opening polymerisation of tetrahydrofuran and is represented by the following general formula:



The organic polyisocyanate is mixed with the above polytetramethylene ether diol at a NCO/OH molar ratio of 5 to 40 and is reacted at about 80° for about 3 hours to obtain a partial prepolymer having an NCO group at the molecular terminal.

The active aromatic polyamine which is the chain extender is preferably one which is hindered by being substituted by at least one alkyl group having 5 or less carbon atoms. Examples of the active aromatic polyamine used as the chain extender and free of the electron attractive group on the aromatic nucleus in the present invention include 4,4'-diaminodiphenyl, 4,4'-diaminodiphenyl ether, 2,3-, 3,4-, 2,4- and 2,6-diaminotoluene or mixtures thereof at various weight ratios, 2,4- and/or 4,4'-diaminodiphenylmethane, 3,3'-diethyl-4,4'-diaminodiphenylmethane, 1,3- and 1,4-phenylenediamine, naphthylene-1,5-diamine, polymethylene polyphenyl polyamine liquid polymer obtained by aniline-formaldehyde condensation, 1,3-dimethyl-2,4-diaminobenzene, 1,3-diethyl-2,4-diaminobenzene, 1,3-dimethyl-2,6-diaminobenzene, 1,4-diethyl-2,5-diaminobenzene, 1-methyl-3,5-diethyl-2,4-diaminobenzene (a), 1-methyl-3,5-diethyl-2,6-diaminobenzene (b), a mixture of (a) and (b) (hereinafter referred to as DETDA), 1,4-diisopropyl-2,5-diaminobenzene, 1,4-dibutyl-2,5-diaminobenzene, 2,4-diaminomesitylene, 1,3,5-triethyl-2,4-diaminobenzene, 1,3,5-triethyl-2,6-diaminobenzene, 1,3,5-triisopropyl-2,4-diaminobenzene and similar compounds, 2,3-dimethyl-1,4-diaminonaphthalene, 2,6-dimethyl-1,5-diaminonaphthalene, 2,6-diisopropyl-1,5-diaminonaphthalene, 2,6-dibutyl-1,5-diaminonaphthalene, 3,3',5,5'-tetramethyl benzidine, 3,3',5,5'-tetra isopropyl benzidine, 3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetrabutyl-4,4'-diaminodiphenylmethane, 3,5-diethyl-3'-methyl-2',4'-diaminodiphenylmethane, 3,5-diisopropyl-3'-methyl-2',4'-diaminodiphenylmethane, 3,3'-diethyl-2,2'-diaminodiphenylmethane, 3,3'-diethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetraethyl-4,4'-diaminodiphenyl ether, and 3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenyl ether. The above aromatic polyamines are used alone or in combination.

The catalyst used in the present invention is a mixture containing an organobismuth compound as an effective ingredient and is prepared by reacting an organic carboxylic acid with a bismuth salt. Bismuth trineodecanoate (Trademark : COSCAT #83 by COSAN CHEMICAL CO., LTD.) is particularly preferred. This compound is represented by the following structural formula :



with about 57 % purity.

A partial prepolymer having a high NCO % and a high NCO/OH molar ratio is so highly active as to have high reactivity with water and to be easily able to foam. However, the use of the above catalyst not only promotes the reaction between isocyanato group and OH group, but also controls the reaction with moisture in the resin and air, resulting in chain extension taking place at an early stage and so initial cheese-like appearance is not observed to exhibit rubber elasticity. As the result, the elastomer thus obtained has a high density. Moreover, the above catalyst is not decomposed at raised temperatures and has good heat resistance.

The catalyst is used in a amount of 0.2 to 2.0 % by weight based on the resin component.

The two components high pressure colliding and mixing spray machine is of such a type that the partial prepolymer component collides with the resin component under high pressure at a blow-off nozzle to be thoroughly mixed with each other and to be dashed and coated onto the application surface, for example, preferably including RIM Series, MODEL T-3 by GLAS-CRAFT, INC., MODEL-II by GUSMER Corp. and the like. These two components high pressure sprayers are such that the stock solutions are sprayed onto the application surface under a blow-off pressure of 60 to 150 kg/cm<sup>2</sup> and a mixture of the stock solutions forms fine particles, resulting in making it possible to obtain an even application surface and to obtain a fairly thick coating by one spraying.

The low molecular weight glycols are used alone or in combination, and in an amount of 1 to 20% by weight based on polytetramethylene ether glycol with the result that the NCO/OH molar ratio between a mixture thereof with polytetramethylene ether glycol and the organic polyisocyanate is in the range of from 5 to 40.

Partial prepolymer is made by a process, for example, as indicated in Rubber Age November, pp 46 - 47 (1973).

Plasticisers which can be mixed with the partial prepolymer component and the resin component include dioctyl phthalate (DOP), dibutyl phthalate (DBP), dioctyl adipate (DOA), and chlorinated paraffin. The plasticiser can be used in an amount of at least 2% by weight, preferably 5 to 10% by weight based on the partial prepolymer component and the resin component.

5 Flame-retardants which can be mixed with the partial prepolymer component and the resin component include phosphoric acid esters such as tris- $\beta$ -chloropropyl phosphate (FYROL PCF by AKZO JAPAN, Ltd.), tris-dichloropropyl phosphate (CRP marketed by DAIHACHI CHEMICALS, Co., Ltd.), tris-chloroethyl phosphate (CLP marketed by DAIHACHI CHEMICALS, Co., Ltd.), and bromine compounds such as tribromoneopentyl alcohol.

10 The above flame-retardant can be used in an amount of at least 2% by weight, preferably 5 to 15% by weight based on the partial prepolymer component and the resin component.

In the present invention, stabilizers, and if necessary organic or inorganic pigments or fillers are also used.

15 Examples of the stabilizer include positionally hindered phenols such as IRGANOX 1010 and 1076, trademark, marketed by CIBA GEIGY Co., Ltd., and YOSHINOX BHT, BB and GSY-930, marketed by YOSHITOMO SEIYAKU Co., Ltd., bezotriazols such as TINUVIN P, 327 and 328, marketed by CIBA GEIGY Co., Ltd., benzophenones such as TOMISOAP 800, marketed by YOSHITOMO SEIYAKU Co., Ltd., and positionally hindered amines such as SANOL LS-770 and 744, TINUVIN 144, marketed by CIBA GEIGY Co., Ltd.

20 The stabilizer is used in an amount of 0.3 to 2% by weight based on the resin component.

Examples of fillers include glass fibre, carbon black, calcium carbonate, talc, kaolin, zeolite, diatomaceous earth, pearlite, vermiculite and titanium dioxide.

The filler is can be used in an amount of 5 to 10% by weight based on the resin component.

In the practice of the present invention, the partial prepolymer is taken as a component A, as it is or by  
25 preferably mixing therewith a proper amount of plasticizer and flame retardant in order to control a flow rate volumetric ratio between two components. On the other hand, component B is formed by mixing polyol, the chain extender, the catalyst, the pigment and the like. The components A and B are blown off at a predetermined flow rate ratio from the two components high pressure spray machine to be sprayed on to the application surface in a molar ratio (NCO/OH) of 0.9 to 1.3, the spraying condition has desirably a  
30 temperature usually 50 to 60°C wherein the viscosity of components A and B which are liquids desirably under 200 cps, and the difference of pressure between both liquids to be normally less than 14 kg/cm<sup>2</sup>. In the case where glass fibre is used as the filler, air is blown off as a chopped strand glass fibre is cut to length at a position of the head of a gun so that the glass fibre is mixed with both components while flying in the air. A mixture of the components A and B, which has been applied on to a coated product, is cured  
35 within one to ten seconds. As desired, the above procedure can be repeated several times to obtain a coated product having a predetermined film thickness.

The spray urethane elastomer according to the present invention can be used in lining or protective coating for iron structures such as for example pipes and tanks, a waterproof coating for materials such as concrete for the roof and outside walls, thick-coated protective coating for a thermal insulant such as rigid  
40 polyurethane foam, polystyrene foam or board, seamless floor covering material, open-mould moulding by use of a mould made of metal or resin.

According to the present invention, spraying only of the stock solutions by use of the two components high pressure spray machine accomplishes coating and the stock solutions are cured in one second to ten and several seconds after being sprayed without producing cells even when thick-coated. Therefore, the  
45 present invention makes it possible to effect wet-on-wet coating within a short period of time, resulting in making it possible to accomplish a coating having a predetermined thickness in a short period of time.

The present invention also makes it possible to accurately reproduce complicated configurations such as an uneven design on the surface of an object to be coated by a simple operation on the surface of the object to be coated, because no cells are formed.

50 The present invention is explained more in detail by the following Examples.

The formulations in the following Examples and Comparative Examples are represented by g(gram).

#### (A) Preparation of partial prepolymer component (Isocyanate component) :

55 To a mixture of purified MDI (MDI-PH, marketed by MITSUI TOATSU CHEMICALS, INC.) and liquid MDI (MDI-LK, marketed by MITSUI TOATSU CHEMICALS, INC.) further including MDI(mixed) in Example 2 and MDI(mixed) only in Comparative Example 2, is added PTMEG, PPG or polyester polyol as shown in Table 1 to be reacted at 80°C for 3 hours in a nitrogen atmosphere, followed by adding assistants such as

flame-retardant and the like to obtain a partial prepolymer component (isocyanate component).

(B) Preparation of resin component :

- 5 The resin component is prepared by uniformly mixing the aforementioned PTMEG, PPG or polyester polyol, the aforementioned DETDA or 1,4-butanediol, the aforementioned COSCAT #83, toner, stabilizer and the like according to the formulations shown in Table 1.

Examples 1 - 3

10

The formulations are as shown in Table 1.

- The partial prepolymer component (solution A) and the resin component (solution B) are sprayed at a volumetric ratio of 1 : 1 to 1 : 2 by use of the following machine. The solutions are sent to a two components high pressure spray machine by a GRACO's supply pump (air-driven 2 : 1, 208-177 type) under an air pressure of 5 Kg/cm<sup>2</sup>.

- 15 The spray machine used is a RIM Series marketed by GLAS-CRAFT INC., and is used under a pressure of about 140 Kg/cm<sup>2</sup> when stopped, and 105 to 119 Kg/cm<sup>2</sup> when sprayed. Temperature control of the solutions is carried out in such a manner that the heat exchanger in the body is set at 50°C for solution A and 60°C for solution B, and the electric current of the hose heater is 4 amperes. A flat chamber (No. 1) and tip (043-25) are mounted on a Probler gun marketed by GLAS-CTAFT, INC. to be used as a spray gun. Spraying is carried out 3 to 5 times by use of a 1 mm thick polypropylene sheet as a mould to obtain a sheet having a thickness of about 2 mm. Temperature and relative humidity under the spray conditions are as shown in Table 1. The sheet thus obtained is cultured for 7 days in a thermostatic chamber at 23°C, followed by being subjected to physical properties measurements according to JIS K-6301.

- 20 The physical properties of the sheet thus obtained are as shown in Table 2. The results of heat resistance test for the sheet obtained in Example 2 are as shown in Table 3.

Comparative Examples 1-6

- 30 Physical properties of the sheets obtained by spraying solution A and solution B according to the formulations in Table 1 respectively under the same conditions as in Examples 1-3 by use of the same two components high pressure spray machine as in Examples 1-3, are as shown in Table 2. The results of heat resistance test for the sheet obtained in Comparative Example 2 are as shown in Table 3.

- 35 As shown in Table 1 to Table 3, the sheets obtained by use of COSCAT #83 catalyst according to the present invention have better physical properties, i.e. modulus, tensile strength, elongation and tear strength compared with those obtained by use of DBTDL catalyst.

The results of the heat resistance test show that the sheets obtained by use of COSCAT #83 catalyst have better physical properties compared with those obtained by use of DBTDL catalyst in all of the above physical properties.

- 40 Even if COSCAT #83 is used, the use of low molecular weight glycol as the chain extender results in reducing the reaction rate to be unapplicable to the spray molding according to the present invention, in showing cheese-like appearance on curing and such undesirable appearance as to cause cracks.

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50

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Table 1  
Formulation (g)

	Example 1	Comp. Ex. 1	Example 2	Comp. Ex. 2	Example 3	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
(A) Partial prepolymer (isocyanate)	777	—	287	—	1,190	—	775	667	687
MDI-PH	333	—	143.5	—	793	—	333	333	172
MDI-LK	—	—	287	287	—	—	—	—	—
MDI (Mixture)	500	500	—	—	384	384	500	—	—
PTMEG-1,000	—	—	324.3	—	—	—	—	—	—
PTMEG-650	—	—	—	—	15.5	—	—	—	—
DPC	—	—	—	—	—	—	—	—	—
PPG-Diol-3000 (OHV:37)	—	—	—	—	—	—	—	570	—
EA-2000 (OHV : 56.1)	—	—	52.1	52.1	—	—	—	—	250
PYROL-PCF (flame-retardant)	—	—	—	—	—	—	—	—	—
(AKZO JAPAN)	19	19	17	—	24	—	19	19	24
NCO% by weight	8.4	8.4	5.6	5.6	15	—	8.4	20	26.5
NCO/OH (mol ratio)	700	700	1,000	1,000	400	400	700	350	600
Viscosity (cPS/25 °C)	1.1	1.1	1.1	1.1	1.15	1.15	1.1	1.18	1.21
Sp. Gravity	—	—	—	—	—	—	—	—	—

Table 1 (to be continued)  
Formulation (g)

	Example 1	Comp. Ex. 1	Example 2	Comp. Ex. 2	Example 3	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
(B) Resin									
PTMEG-1,000	66.6	+	-	-	-	-	66.6	-	-
PTMEG-1,500	-	-	-	-	75.8	+	-	-	-
PTMEG-650	-	-	79.2	+	-	-	-	-	-
DETDA	28.4	+	15.3	+	18.7	+	28.4	-	-
PPG-Diol-2000 (OHV:56)								73.2	-
EA-2000 (OHV):56.1								-	67.5
1,4-BD								21.8	21.5
TINUVIN® 9327 (Stabilizer)								0.5	-
DOP								-	6.0
DBTDL (Catalyst)	-	1.0	-	1.0	-	1.0	(PB-Naphthenate (24X)) 1.0	-	-
COSCAT® 483 (Catalyst)	0.5	-	0.5	-	0.5	-	-	0.5	0.5
Toner	4.5	4.0	5.0	4.5	5.0	4.5	4.0	4.0	4.0
IRGANOX® 1010 (Stabilizer)	0.5	+	0.5	+	0.5	+	0.5	-	0.5
(CIBA CEIGY CO.)									
MCO INDEX: (MCO/OH (molar ratio))	1.1	+	1.05	+	1.05	+	1.1	1.1	1.1
(in curing)									
Formulation Ratio	1/1	+	1/1	+	1/2	+	1/1	1/1.5	1/2
Volume (A)/(B)									



Table 1 (concluded)

	Example 1	Example 2	Comp. Ex. 2	Example 3	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
in molding Temperature (°C) Relative humidity (RH) (%)	6.3 30	27.8 68	— —	23 55	— —	6.3 30	— —	23 55
Moldability							Reaction is late. liquid hangs down when applied on vertical surface	—
Curability							When curing, it develops into a shape like weakly coagulated cheese. it takes time to produce physical properties	—

## Note :

EA-2000 Polyesterpolyol of Ethylene glycol and Adipic acid  
 1,4-BD 1,4-Butanediol  
 OHV Hydroxyl value  
 MDI-PH Pure MDI (4,4'-isomer: over 98%)  
 MDI-LK Liquid MDI, Carbodiimide modified  
 MDI (mixture) 4,4'-isomer + 2,4'-isomer (60/40 % by weight)  
 PNEG-1,500 Polytetramethylene ether glycol, Mol. Weight: ca. 1,500  
 PNEG-1,000 Polytetramethylene ether glycol, Mol. Weight: ca. 1,000  
 PNEG-650 Polytetramethylene ether glycol, Mol. Weight: ca. 650  
 DPG Dipropylene glycol  
 DETDA Mixture of 1-methyl-3,5-diethyl-2,4-diamino benzene and  
 1-methyl-3,5-diethyl-2,6-diaminobenzene (chain extender)  
 DBTDL Dibutyl tin dilaurate (catalyst)  
 Toner Mixed and kneaded material of inorganic and/or organic pigment  
 and plasticizer

Table 2 Physical property (thickness: ca. 2 mm)

	Example 1	Comp. Ex. 1	Example 2	Comp. Ex. 2	Example 3	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
Density (g/cm <sup>3</sup> )	0.99	0.86	0.98	0.80	0.99	0.76	Molded sheet develops into a shape like weakly coagulated cheese, disabling it to measure physical properties.	0.84	0.73
Hardness	59D	51D	97A	91A	93A	86A		85A	82A
M <sub>100</sub> (Kg f/cm <sup>2</sup> )	146	118	130	83	92	63		65	58
Tensile strength (Kg f/cm <sup>2</sup> )	240	154	250	180	230	145		95	80
Elongation (%)	260	170	280	200	340	270		380	240
Tear strength (Kg f/cm <sup>2</sup> )	85	70	77	64	69	53		45	42

Note :

Hardness (D: Shore-D, A: Shore-A)

M<sub>100</sub> 100% tensile modulus

Table 3 Heat resistance test (Maintenance of physical property X)

## (1) COSCAT 483 Catalyst (Sheet of Example 2)

	Hardness	M <sub>100</sub>	Tensile strength	Elongation	Tear strength
Blank test	100	100	100	100	100
after 70°C×7 days	100	106	109	100	100
after 100 °C×7 days	101	98	109	115	104
after 120 °C×7 days	98	88	109	138	117

## (2) DBTDL Catalyst (Sheet of Comparative Example 2)

	Hardness	M <sub>100</sub>	Tensile strength	Elongation	Tear strength
Blank test	100	100	100	100	100
after 70°C×7 days	112	103	112	123	104
after 100 °C×7 days	104	80	54	100	81
after 120 °C×7 days	83	-	31	9	38

## Claims

1. A process for manufacturing a solventless spray urethane elastomer which comprises spraying directly onto a substrate, by use of a two components high pressure spray machine with a colliding and mixing type spray gun under a pressure of 60 to 150 kg/cm<sup>2</sup>, in a NCO/OH molar ratio of 0.9 to 1.3 of the

undermentioned components A and B:

- 5 component A - a partial prepolymer component prepared by reacting an organic polyisocyanate and a polytetramethylene ether glycol having a molecular weight of 400 to 2000 or a mixture of polyols which consists of the polytetramethylene ether glycol and from 1 to 20% by weight of the polytetramethylene ether glycol of a low molecular weight glycol selected from dipropylene glycol, tri propylene glycol, tetrapropylene glycol, diethylene glycol, 1,3-butanediol, 1,4-butanediol and neopentylglycol, at a NCO/OH molar ratio of 5 to 40,
- 10 component B - a resin component prepared by mixing a polytetramethylene ether glycol having a molecular weight of 400 to 2000, a chain extender which consists of an active aromatic polyamine which is free of an electron attractive group on the aromatic nucleus, an organobismuth compound as a catalyst,
- and optionally, one or more of:
    - 15 (i) one or more plasticizers selected from dioctyl phthalate, dibutyl phthalate, dioctyl adipate, and chlorinated paraffin,
    - (ii) one or more flame-retardants selected from phosphoric acid esters and bromine compounds,
    - (iii) a stabiliser in an amount of from 0.3 to 2% by weight of the resin component, and/or
    - 20 (iv) a filler,
- the proportion of glycol being at least 70% by weight, of polyamine being at least 10% by weight, and of catalyst being from 0.2 to 2% by weight.
2. A process as claimed in Claim 1 in which the polyisocyanate is a purified or crude diphenylmethane diisocyanate, or modified diphenylmethane diisocyanate.
3. A process as claimed in Claim 1 or Claim 2 in which the organobismuth compound is bismuth trineodecanoate.
- 30 4. A process as claimed in any preceding claim in which the flame-retardant is tris- $\beta$ -chloropropyl phosphate, tris-dichloropropyl phosphate and/or tris-chloroethyl phosphate, and/or tribromoneopentyl alcohol.

# Patentansprüche

- 35 1. Verfahren zur Herstellung eines lösungsmittelfreien Spritz-Urethanelastomers, das das direkte Spritzen der nachstehenden Komponenten A und B in einem NCO/OH-Molverhältnis von 0,9 bis 1,3, wobei es sich bei
- 40 Komponente A um ein partielles Vorpolymer handelt, das hergestellt wird durch Umsetzen eines organischen Polyisocyanats und eines Polytetramethylenetherglykols mit einer relativen Molekülmasse von 400 bis 2000 oder eines Polyolgemisches aus dem Polytetramethylenetherglykol und 1 bis 20 Masse-% des Polytetramethylenetherglykols eines unter Dipropylenglykol, Tripropylenglykol, Tetrapropylenglykol, Diethylenglykol, 1,3-Butandiol, 1,4-Butandiol und Neopentylglykol ausgewählten Glykols mit geringer Molekülmasse in einem NCO/OH-Molverhältnis von 5 bis 40, und bei
- 45 Komponente B um ein Harz handelt, das hergestellt wird durch Mischen eines Polytetramethylenetherglykols mit einer relativen Molekülmasse von 400 bis 2000, eines von einer elektronenanziehenden Gruppe am aromatischen Kern freien aktiven aromatischen Polyamins als Kettenverlängerer, einer bismutorganischen Verbindung als Katalysator,
- 50 - und wahlweise einer oder mehrerer der folgenden Verbindungen:
- i) ein oder mehrere unter Dioctylphthalat, Dibutylphthalat, Dioctyladipat und Chlorparaffin ausgewählte Weichmacher,
  - 55 ii) ein oder mehrere unter Phosphorsäureestern und Bromverbindungen ausgewählte Flammenschutzmittel,
  - iii) ein Stabilisator in einer Menge von 0,3 bis 2 Masse-% der Harzkomponente und/oder

- iv) ein Füllstoff,  
wobei der Glykolanteil mindestens 70 Masse-%, der Polyaminanteil mindestens 10 Masse-% und der Katalysatoranteil 0,2 bis 2 Masse-% beträgt,  
unter Verwendung eines Zweikomponenten-Hochdruck-Spritzgeräts mit einer vereinigenden und mischenden Spritzpistole bei einem Druck von 60 bis 150 kg/cm<sup>2</sup> auf einen Träger umfaßt.
2. Verfahren nach Anspruch 1, wobei das Polyisocyanat ein gereinigtes oder reines Diphenylmethandiisocyanat oder modifiziertes Diphenylmethandiisocyanat ist.
3. Verfahren nach Anspruch 1 oder 2, wobei es sich bei der bismutorganischen Verbindung um Bismuttrineodecanoat handelt.
4. Verfahren nach einem der vorstehenden Ansprüche, wobei das Flammenschutzmittel Tris- $\beta$ -chlorpropylphosphat, Trisdichlorpropylphosphat und/oder Trischlorethylphosphat und/oder Tribromneopentylalkohol ist.

### Revendications

1. Procédé de fabrication d'un élastomère d'uréthane à pulvériser, sans solvant, comprenant la pulvérisation directe sur un substrat à l'aide d'une machine de pulvérisation à haute pression à deux composants, ayant un pistolet de pulvérisation de type à collision et à mélange sous une pression allant de 60 à 150 Kg/cm<sup>2</sup>, selon un rapport molaire NCO/OH allant de 0,9 à 1,3 des composants A et B mentionnés ci-après :
- composant A - un composant prépolymère partiel préparé par la mise en réaction d'un polyisocyanate organique avec un polytétraméthylène éther glycol ayant un poids moléculaire allant de 400 à 2000 ou un mélange de polyols consistant en le polytétraméthylène éther glycol et contenant de 1 à 20 % en poids de polytétraméthylène éther glycol, composé d'un glycol à faible poids moléculaire sélectionné dans le groupe composé du dipropylène glycol, tripropylène glycol, tétrapropylène glycol, diéthylène glycol, 1,3-butanediol, 1,4-butanediol et néopentylglycol, selon un rapport molaire NCO/OH allant de 5 à 40,
- composant B - un composant de résine préparé par le mélange d'un polytétraméthylène éther glycol ayant un poids moléculaire allant de 400 à 2000, d'un diluant de chaîne consistant en une polyamine aromatique active ne comportant pas de groupe attirant les électrons sur le noyau aromatique d'un composé organobismuth à titre de catalyseur - et en option, un ou plusieurs éléments parmi :
- (i) un ou plusieurs plastifiants sélectionnés parmi le dioctyle phthalate, le dibutyle phthalate, le dioctyle adipate et la paraffine chlorée,
- (ii) un ou plusieurs agents retardateurs de flamme sélectionnés parmi les esters d'acide phosphorique et les composés du brome,
- (iii) un stabilisant en une quantité allant de 0,3 à 2 % en poids du composant de résine, et/ou
- (iv) un agent de remplissage,
- la proportion de glycol étant au moins de 70 % en poids, celle de la polyamine étant au moins de 10 % en poids et celle du catalyseur ayant une valeur allant de 0,2 à 2 % en poids.
2. Procédé selon la revendication 1, dans lequel le polyisocyanate est un diphenylméthane diisocyanate purifié ou brut.
3. Procédé selon la revendication 1 ou la revendication 2 dans lequel le composé organobismuth est du trinéodécanoate de bismuth.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le retardateur de flamme est un tris- $\beta$ -chlorpropyle phosphate, un tris-dichloropropyle phosphate et/ou un tris-chloroéthyle phosphate et/ou un tribromnéopentyle alcool.